THE PROPERTIES OF MORTAR USING BLENDS WITH PORTLAND CEMENT CLINKER, ZEOLITE TUFF AND GYPSUM

IVAN JANOTKA, ĽUDOVÍT KRAJČI

Institute of Construction and Architecture,
Slovak Academy of Sciences,
Dúbravská cesta 9, 842 20 Bratislava, Slovak Republic

Received 31. 7. 1995

This paper deals with the properties of mortars containing the mixtures of Portland cement clinker, zeolite tuff and gypsum. The mortars consisting of mixtures with 87.42 to 87.99 % of Portland cement clinker, 9.62 to 9.99 % zeolite tuff and 2.02 to 5.63 % of gypsum were prepared and compared to zeolite - free control mortar with 95.2 % of Portland cement clinker and 4.98 % of gypsum. The 1 095 day compressive strength of zeolite-modified mortars is comparable to that in the control one. Contemporarily a portion of micropores with radius less than 100 nm in the pore structure of zeolite-modified mortars is larger than in the control one. The presence of zeolite tuff in the mortars has not negative effect on steel corrosion.

INTRODUCTION

The activity of pozzolanic materials is characterized by their absolute susceptibility to combine with CaO and its reaction kinetics with $Ca(OH)_2$ in the presence of water under normal temperature [1]. In zeolite tuff+ $Ca(OH)_2$ binder pastes 2:1 and 1:1 hydration products of C-S-H gel and tobermorite were distinguished whereas binder paste of zeolite tuff + C_3A gives hydration products of C_3AH_6 and hydrogarnet phase [2]. Due to the zeolite tuff the process of bonding of SO_3 in the Portland cement mortar is considerably slowned down and thereby the resistance of the mortar against action of 55 percent solution of Na_2SO_4 during 510 day's cure is substantially increased [3]. By replacing parts of clay with finely ground zeolite tuff considerable improvement of corrosion resistance of cement suspension used in underground sealing wall in Verneřov (Czech Republic) was achieved when contacted with an aggressive water containing in average 2 000 mg l^{-1} of sulfates and having a pH value of 4.5 [4].

It was found that ordinary Portland cements without gypsum as regulator of setting are characterized by an accelerated setting time and high early strength when Portland clinker is ground to a specific surface area of 400 - 550 m^2 kg^{-1} in the presence of efficient grinding aids [5]. Gypsum-free pastes of ground Portland cement clinker tend to harden very rapidly generating considerable heat of hydration. At present an attention is devoted to ground Portland cement clinker with the replacement of the function of gypsum by other substances [6,7,8,9]. In most cases, the added modifiers retard the setting time of Portland cement pastes without gypsum addition to cement and decrease the compressive strength compared to unmodified control specimens.

Six blends with Portland cement clinker, zeolite tuff and gypsum are introduced and compared to the Portland cement properties in this paper. The main aim of this work is to compare physico-mechanical properties, phase composition and pore structure of modified mortars with that without zeolite tuff addition. The ability of mortars to protect steel reinforcement against corrosion was verified too.

EXPERIMENTAL PART

Materials

Ordinary Portland cement of class 400 and sand specified in ČSN 72 1208 Standard [10] were used in all mixes. An aliquot portion of the Portland cement clinker was replaced by zeolite tuff. The composition of the zeolite-modified cement clinker was adjusted to 100 % of dry constituents by the $CaSO_4.2H_2O$ addition. The properties of the employed cement and composition of cement mixtures manufactured in ZEOCEM cement works, Bystré nad Topľou, Slovakia are given in Table I and Table II. Commercial zeolite tuff was used as cement modifier. Its properties are listed in Table III.

Table I. Composition and properties of the Portland cement employed

Component content (wt.%)		Content of major clinker phases according to Bogue (%)	
Insoluble residue	1.63	C_3S	49.45
SiO_2	20.64	C_2S	21.88
Al_2O_3	5.88	C_3A	10.28
Fe_2O_3	3.13	C_4AF	9.53
CaO	61.49	Specific gravity	3 140 kg m^{-3}
MgO	1.34	Specific surface area	336.2 m^2 kg^{-1}
SO_3	2.30	Beginning of setting	3 hours 15 minutes
K_2O	1.82	Setting time	4 hours 20 minutes
Na_2O	0.53	3 day cement strength:	flexural/ /compressive 4.4 / 23.5 MPa
Ignition loss	1.04	28 day cement strength:	flexural/ /compressive 7.9 / 41.7 MPa

Table II. Properties of cement mixtures based on zeolite tuff addition to Portland cement clinker

Cement property		Cement mixtures 1	2	3	4	5	6
Beginning of setting (hr/min)		0/40	1/20	1/40	2/35	2/15	0/35
Setting time (hr/min)		1/25	3/45	3/15	3/30	4/40	1/25
Ignition loss (%)		9.20	5.59	5.63	8.88	6.27	7.06
Content of SO_3 (%)		1.60	1.18	1.74	2.62	0.94	1.59
Content of CaO (%)		51.03	54.67	54.39	50.75	54.67	53.55
Standard strength (MPa)	flexural[1)]						
	3 days	2.9	2.7	4.2	3.4	3.3	3.6
	28 days	6.8	7.0	8.0	7.1	5.3	7.6
	compressive[2)]						
	3 days	11.4	9.0	16.5	12.7	14.6	14.2
	28 days	26.7	31.4	33.5	28.9	23.1	31.3
Residue on fine -mesh screen (wt.%)							
	0.2 mm	0.2	0.2	1.3	0.4	0.1	0.1
	0.09 mm	3.5	1.8	6.5	7.6	0.9	1.4

[1) 2)] Standard strength was determined according to ČSN 72 2117 Standard

Table III. Composition and properties of zeolite tuff

Chemical composition (wt.%)	
Ignition loss	1(
SiO_2	6(
CaO	5
MgO	0
Al_2O_3	14
Fe_2O_3	1
SO_3	0.
Humidity of zeolite tuff (wt.%)	4.78
Specific gravity (kg m^{-3})	2 283.7
Specific surface area (m^2 kg^{-1})	1 150.5

Experimental method

Control mortar (C) and zeolite-modified mort (M1 - M6) were prepared using mix proportions given Table IV. Mortar specimens having size of 40 x 40 x 1 mm were moulded and cured 28 days at 20 °C/95 R.H. - moist and then in water for 1 095 days also 20 °C. By the contrast with it cement mixtures w 79 % of Portland cement clinker, 15 % of zeolite tu 6 % of gypsum and 83 % of Portland cement clinke 15 % of zeolite tuff, 2 % of gypsum were verified to Plasticity of the mortars was adjusted to 160 mm ± 5 m according to ČSN 72 2441 [11]. The mortar specime were tested for compressive and flexural strengt dynamic modulus of elasticity, absorption capacity ar total porosity. Absorption capacity was estimated b weighing of mortar specimens permeated with water an then dried at 105 °C. The calculation is based o differences in weight of water saturated and dried morta specimen. Total porosity of mortars was calculated o basis of estimated specific gravity and volume density.

Pore structure of mortar specimens was studied b means of high-pressure mercury porosimeter mod. 200 and macroporosimetry unit 120 (both Erba Science Milan). This apparatus enables to estimate pore radiu between 3.75 nm and 0.2 mm.

The phase composition of the mortars were estimated by X-ray diffractograph Philips using CuK_α radiation and thermal analysis apparatus Derivatograph Q 1 500, MOM Budapest.

Table IV. Mix proportion of mortars with cement mixtures

Cement : sand (by weight)		Composition of mixtures			WC
		clinker (wt.%)	zeolite (wt.%)	gypsum (wt.%)	
	C	95.02	-	4.99	0.33
	M1	86.70	9.86	3.44	0.38
	M2	87.64	9.82	2.54	0.38
1:1.5	M3	86.64	9.62	3.74	0.38
	M4	84.42	9.95	5.63	0.38
	M5	87.99	9.99	2.02	0.38
	M6	86.97	9.62	3.41	0.38

Corrosion of steel was tested in mortar extracts by potentiodynamic method according to ČSN 73 1341 Standard [12].For corrosion tests steel bar of class 10 425 with diameter 6 mm was used. Potentiodynamic curves of steel were obtained by Potentiostat OH 405 (Radelkis Budapest) under polarisation rate 30 mV min^{-1}.

RESULTS AND DISCUSSION

Due to similarity in composition of M1 - M6 cement mixtures the rate of setting is not affected significantly by the content of gypsum in amount of 2.02 - 5.64 %. When the zeolite tuff content is enhanced to 15 wt.% distinct changes in setting time of cement mixtures were observed. The setting time of the mixture with 2 % of gypsum is less than 45 minutes and the beginning of setting was prolonged up to 5 hours and 5 minutes in the cement mixture with 6 % of gypsum. The 15 % content of zeolite tuff in the cement mixtures worsens markedly compressive strength of the mortars. The 28-day compressive strengths varied between 11.8 and 14.6 MPa. This invention into the cement mixture composition compared to that with 10 % content of zeolite tuff evoked unwishful changes in setting characteristics of cement mixtures and distinct decrease in compressive strength of mortar specimens.Therefore further tests with cement mixtures containing 15 % content of zeolite tuff were not carried out. Figure 1 exhibits compressive strength of control mortar and zeolite-modified mortars versus curing period before and after water immersion. The effect of cement composition on compressive strength of mortars is hardly recognized. The compressive strength of modified mortars after water immersion rises with an increase in the fineness of cement mixtures and decrease in gypsum content of cement mixture. Figure 2 illustrates the flexural strength of mortars versus curing period before and after water immersion. In both cases, the strength loss of zeolite-modified mortars in comparison with control one is caused by partial replacement of Portland cement clinker by aliquot portion of zeolite tuff and gypsum.

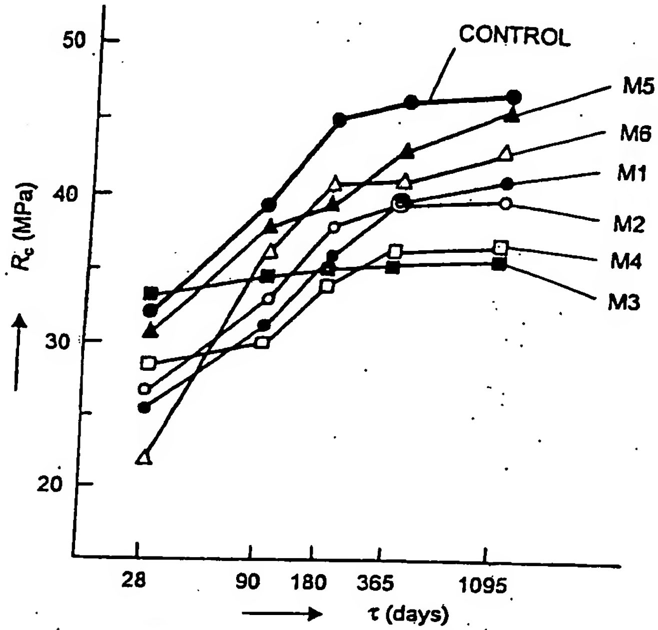

Figure 1. Compressive strength of mortars vs. curing period in water

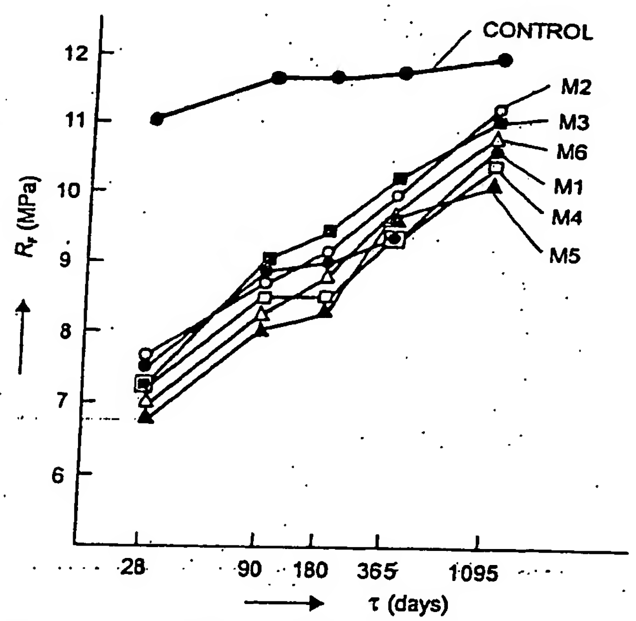

Figure 2. Flexural strength of mortars vs. curing period in water

Table V represents the relationship of dynamic modulus of elasticity, absorption capacity and total porosity of mortars versus curing period. Differences in dynamic modulus of elasticity in tested mortars are of negligible importance. Absorption capacity and total porosity of control mortar is about a one fifth to one third of those in zeolite-modified mortars. The effect of

zeolite tuff on absorption capacity and total porosity of mortars placed 1095 days underwater is much the same as those on the flexural strength of zeolite-modified mortars. These mortar properties are worsened.

Table V. Dynamic modulus of elasticity, absorption capacity and total porosity of mortar specimens cured 1 095 days in water at 20 °C

Type of mortar	Dynamic modulus of elasticity (GPa)	Absorption capacity (wt.%)	Total porosity according to ČSN 72 2447 (vol.%)
Control	30.8	7.0	13.3
M1	31.1	10.5	18.9
M2	30.9	10.4	16.5
M3	30.3	11.0	16.5
M4	31.2	10.5	15.2
M5	30.7	11.8	15.9
M6	31.2	11.4	15.7

Comparison of the results of porosimetric analysis specified in Table VI and Table VII shows that median pore radius and pore size distribution of mortar specimens depend decisively on the cement composition. Pore size distribution in the mortars containing zeolite tuff is markedly different compared to that in the control mortar. The portion of micropores with radius less than 100 nm is enhanced when cement clinker is partially replaced by zeolite tuff. This phenomenon is caused by higher fineness of zeolite tuff.

The relative content of $Ca(OH)_2$ and main clinker minerals of mortars were determined by comparing the characteristic diffraction intensities (Figures 3 and 4). The presence of $Ca(OH)_2$ is detected by diffraction intensities of 4.92 Å ; 3.11 Å, 2.63 Å, 1.92 Å and 1.79 Å. The relative amount of unreacted alite and belite is characterized by the doublet at 2.78 Å and 2.74 Å. Diffraction intensities 3.86 Å, 3.03 Å, 2.09 Å and 1.87 Å belong to $CaCO_3$. The remaining correspond to SiO_2.

Table VI. Results of pore structure study of mortar specimens cured 1095 days in water at 20 °C

Type of mortar	Volume of micropores (%)	Median of pore radius (nm)	Porosity according to Hg - porosimetry (%)
Control	90.10	46.99	10.40
M1	95.38	49.92	13.05
M2	94.10	52.38	13.52
M3	96.58	49.57	13.35
M4	92.00	39.00	14.42
M5	95.30	49.20	15.47
M6	94.67	43.46	15.08

Table VII. Pore size distribution in mortar specimens cur days in water at 20 °C

Pore radius	Pore size distribution (%)					
	control	M1	M2	M3	M4	M5
to 50 nm	44.59	50.82	46.89	49.87	60.05	52.1
50-100 nm	25.93	29.58	32.97	37.40	18.08	29.5
100-1000 nm	14.52	12.89	12.45	7.21	6.51	11.31
1000-3000 nm	4.14	0.76	2.19	1.91	2.17	1.25
3000-7500 nm	2.08	1.51	0.74	1.13	4.34	1.57
to 7500 nm (micropores)	91.26	95.56	95.24	97.52	91.15	95.83
over 7500 nm (macropores)	8.73	4.43	4.75	2.48	8.83	4.14

The content of $Ca(OH)_2$ is slightly higher i control mortar than in those containing zeolite tuff reason lies in lesser amount of CaO in the ce mixture modified by zeolite tuff and also in suscepti of zeolite tuff to combine with CaO due to its pozzc origin. By the contrast with it modification of ce mixture by zeolite tuff results in a slight increa $CaCO_3$ content. Cement mixture modified by zeolite has a similar effect on the hydration of the cement of mortar specimens as revealed by mildly decre content of $Ca(OH)_2$ and roughly equal diffra intensities of uncreacted alite and belite compared tc prepared from Portland cement.

These interesting facts follow from the result thermal analysis (Table VIII). A relative high conte bound water in hardened cement paste is typical fo cured mortars. The amount of bound water zeolite-modified mortars is affected by the zeolite content in cement mixtures. However, the 10 % cor of zeolite tuff does not influence markedly bound w content in the hydrate phase of mortar specin between temperature 100 and 420 °C. With respect tc 10 % replacement of Portland cement clinker by ze tuff in cement mixtures total content of CaO bound $Ca(OH)_2$ and $CaCO_3$ in zeolite-modified mortars slightly lower than that in the control mortar. The rea lies in the lower CaO content in the composition of M6 cement mixtures than that of Portland cement.

The corrosion characteristics of steel in mo extracts obtained by potentiodynamic method are gi in Table IX. The course of potentiodynamic curves steel is shown in Figure 5. Differences in values current density of passivation, potential of break-dowr well as in pH of mortar extracts between zeolite-modif mortars and control one are of negligible importance. T steel is always in the passive state. The achieved resu confirm that zeolite tuff in cement mixture does initiate the corrosion of steel in the mortars.

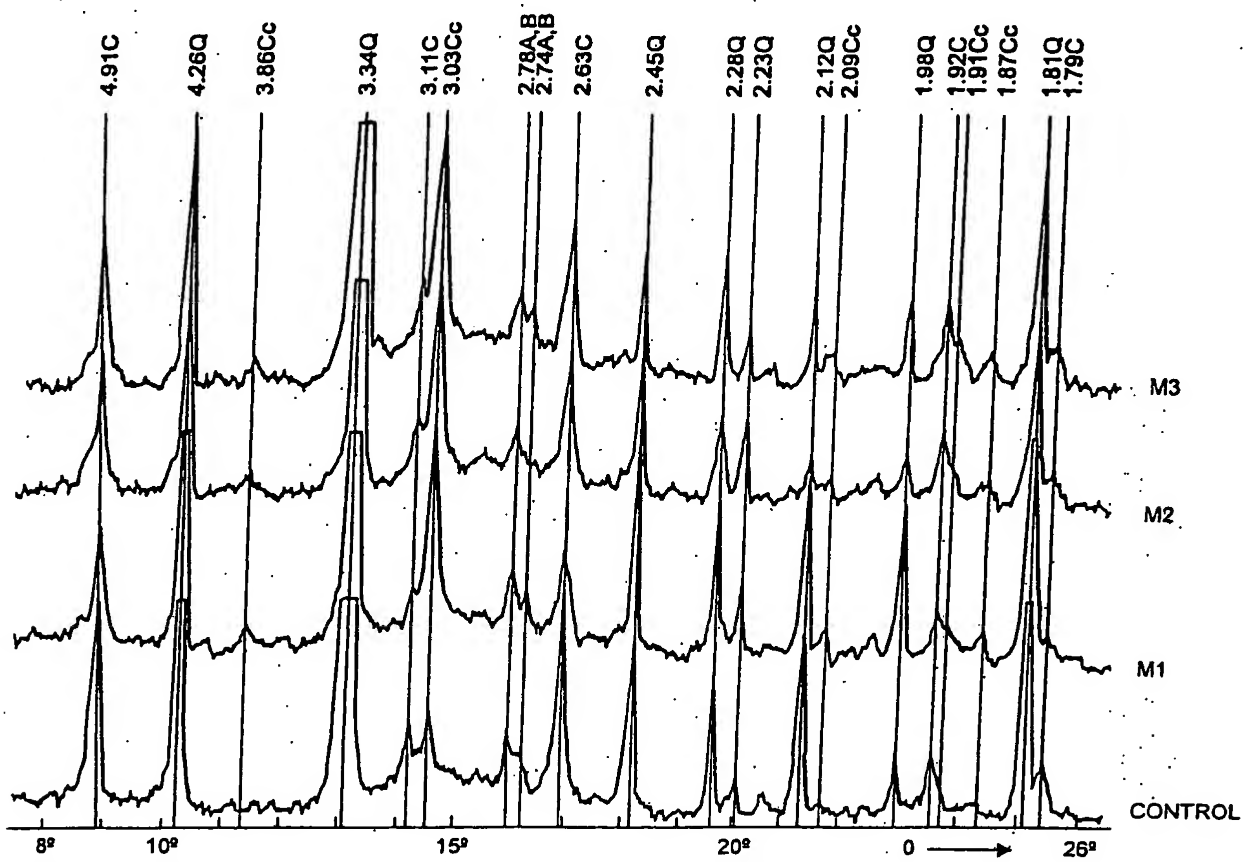

Figure 3. X-ray diffraction patterns of tested mortars cured 1 095 days in water at 20 °C

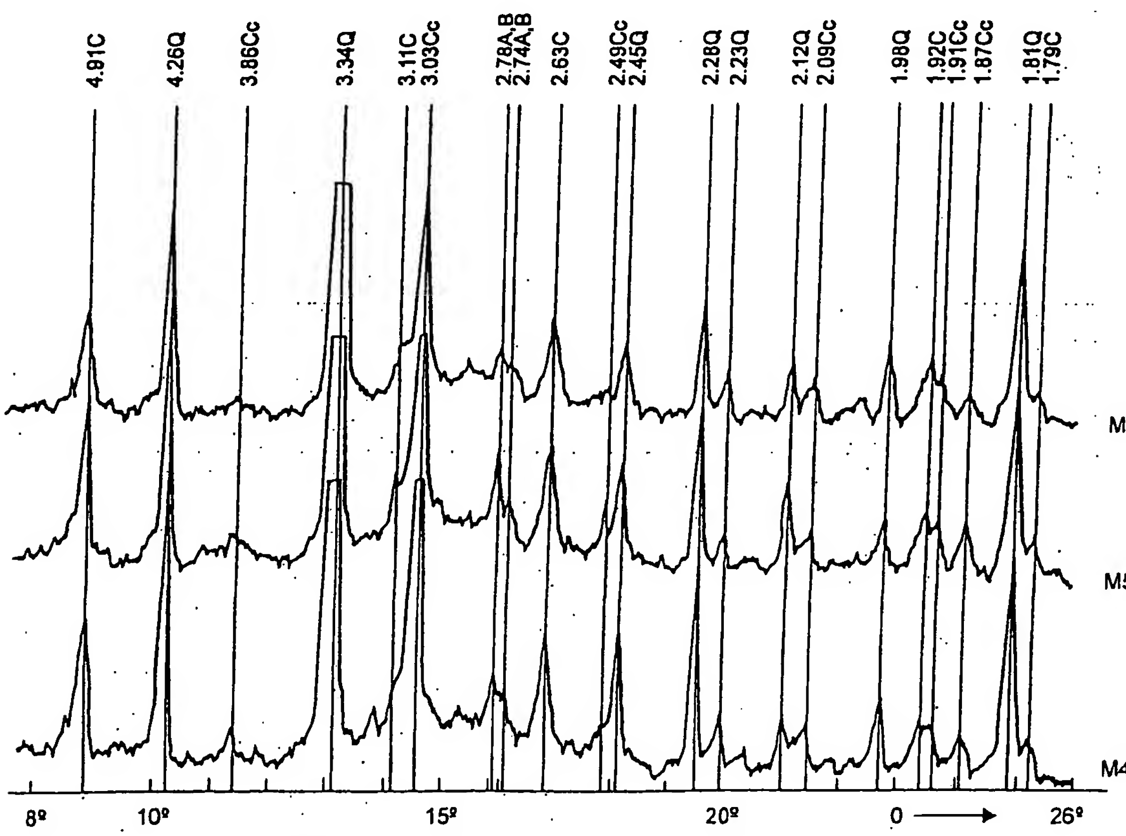

Figure 4. X-ray diffraction patterns of tested mortars cured 1 095 days in water at 20 °C

Table VIII. Results of thermal analysis of tested mortars cured 1 095 days in water at 20 °C

Type of mortar	Ignition loss to 420 °C (%)	Ignition loss to 1 000 °C (%)	CaO bound in $Ca(OH)_2$ (%)	CaO bound in $CaCO_3$ (%)	Total content of CaO in $Ca(OH)_2$ and C (%)
Control	6.30	15.71	1.89	2.56	4.45
M1	5.26	14.22	1.32	2.63	3.95
M2	7.36	16.98	1.57	2.64	4.21
M3	6.04	14.58	0.94	2.29	3.23
M4	6.00	16.09	1.40	3.12	4.32
M5	8.48	18.20	1.44	2.83	4.27
M6	6.84	15.53	1.19	2.95	4.14

Table IX. Corrosion characteristics of steel of mortars cured 1 095 days in water at 20 °C

Type of mortar	Stationary potential (mV)	Current density of passivation ($A\ m^{-2}$)	Potential of break - down (mV)	State of reinforcement	pH of extract
Control	-330	0.031	570	passive	12.47
M1	-330	0.029	570	passive	12.40
M2	-330	0.030	575	passive	12.47
M3	-330	0.033	575	passive	12.41
M4	-330	0.029	560	passive	12.43
M5	-330	0.026	565	passive	12.45
M6	-330	0.026	565	passive	12.42

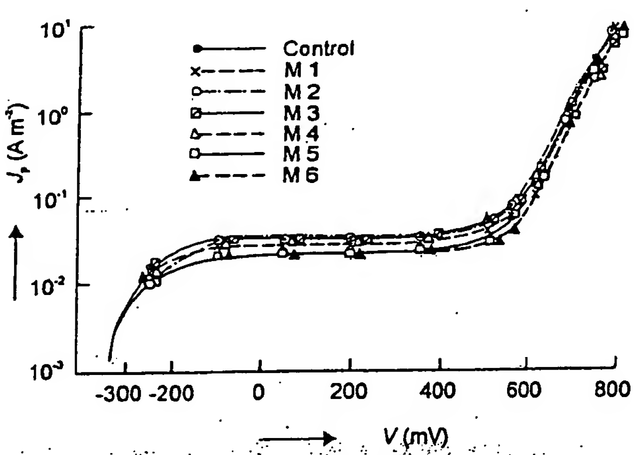

Figure 5. Potentiodynamic curves of steel in extract of cured mortars (current density vs. potential of steel)

CONCLUSIONS

1. The beginning of setting and setting time of cement mixtures M1 - M6 consisting of Portland cement clinker, zeolite tuff and gypsum are accelerated markedly in comparison with that of Portland cement. When cer mixture contains 15 % of zeolite tuff set characteristics depend significantly on gypsum conter the cement mixture.

2. The compressive strength of the control mortar a 1 095 days of water immersion is slightly higher t those prepared from cement mixtures containing up 10 % of zeolite tuff. Compressive strength zeolite-modified mortars is enhanced with increas fineness of cement mixture and decreasing gyps content in cement mixture M1-M6. A significant stren loss of the mortars containing 15 % of zeolite tuff w observed.

3. A large portion of micropores with radius less th 100 nm is a typical feature of the pore structure zeolite-modified mortars. The higher relati representation of micropores in mortars containing zeoli tuff than that in the control one is caused by high fineness of zeolite tuff.

4. Both, hydration of the control and zeolite-modifie mortars advances sufficiently. Cement mixture modifie by zeolite tuff does not affect significantly the degree : hydration. A lesser content of CaO bound in $Ca(OH)_2$ an $CaCO_3$ in mortar containing zeolite tuff is caused by th lower CaO content in cement mixtures with zeolite tu than that containing Portland cement.

5. The replacement of the Portland cement clinker by zeolite tuff up to 10 % in cement mixture has no negative effect on the ability of mortars to protect steel against corrosion.

6. The mentioned cement mixtures have been experimentally manufactured in the cement factory already. From this viewpoint the verification of their properties and properties of mortars made from these blends seems to be of great importance. The investigation of zeolite-modified mortars exposed to different liquid aggressive media is just going on.

References

1. Jambor J.: Stavebnícky časopis *IX*, 628 (1961)
2. Jambor J.: Stavebnícky časopis *XVIII*, 464 (1970)
3. Jambor J.: Stavebnícky časopis *XIV*, 511 (1966)
4. Janotka I., Špaček A., Jeřábek M.: Stavebnícky časopis *40*, 681 (1992)
5. Hrazdíra J.: Ceram-Silik *36*, 87 (1992)
6. Škvára F.: Ceram-Silik *36*, 61 (1992)
7. Škvára F., Všetečka T.: Stavivo *67*, 262 (1989)
8. Hrazdíra J.: Ceram-Silik *36*, 149 (1992)
9. Bentur A., Kovler K., Goldman A.: Advances in Cement Research *6*, 109 (1994)
10. ČSN 72 1208 Testing sands
11. ČSN 72 2441 Testing of workability of fresh mortars
12. ČSN 73 1341 Corrosion protection of reinforcements provided by the properties of concrete. Methods of test

Submitted in English by the authors

VLASTNOSTI MÁLT ZA POUŽITIA ZMESÍ Z PORTLANDSKÉHO SLINKU, ZEOLITOVÉHO TUFU A SADROVCA

IVAN JANOTKA, ĽUDOVÍT KRAJČI

Ústav stavebníctva a architektúry SAV, Dúbravská cesta 9, 842 20 Bratislava

Prešetrovali sa cementové zmesi s rozdielnou dávkou Portlandského slinku, zeolitového tufu a sadrovca. Ku skúškam sa použili malty s hmotnostným pomerom cementovej zmesi a piesku 1:1.5 s plasticitou 160 ± 5 mm. Malty sa ošetrovali 1 095 dní vo vode s teplotou 20 ± 2 °C. Účinok rôzneho zloženia cementových zmesí sa preveroval z hľadiska pevností, fázového zloženia, pórovej štruktúry a pasivačných vlastností mált.

Zo štúdia cementových zmesí a mált vyplývajú nasledovné poznatky:

- počiatok a doba tuhnutia cementových zmesí s prídavkom zeolitového tufu sa mení v závislosti od dávky sadrovca, vo väčšine prípadov sa však skracuje v porovnaní s počiatkom a dobou tuhnutia Portlandského cementu,
- pevnosť v ťahu ohybom a pevnosť v tlaku mált zhotovených z cementových zmesí je nižšia ako malty s Portlandským cementom,
- vyššia jemnosť zeolitového tufu a nižší obsah sadrovca v cementovej zmesi spôsobujú nárast pevnosti v tlaku mált,
- hydratácia cementových zmesí a Portlandského cementu má podobný priebeh, v maltách so zeolitovým tufom je vyšší podiel mikropórov s polomerom menším ako 100 nm,
- náhrada Portlandského slinku zeolitovým tufom do 10 % hmot. v cementovej zmesi nemá negatívny účinok na schopnosť malty chrániť oceľovú výstuž pred koróziou.

THIS PAGE BLANK (USPTO)